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Interaction of hydrogen with TaC(111) and NbC(111) surfaces: Angle-resolved photoemission study

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Angle-resolved photoemission spectroscopy utilizing synchrotron radiation has been used to study the interaction of hydrogen with TaC(111) and NbC(111) surfaces. The electronic structures of the TaC(111) and NbC(111) clean surfaces are characterized by the surface-induced state at just below the Fermi level. Hydrogen adsorption induces the shift of the state to the higher-binding-energy side by ~0.5 eV at the $\bar{\Gamma}$ point for both surfaces. However, no H 1*s*–induced split-off state is found in the photoemission spectra for both surfaces. This invisible state is proposed to be an adsorption in a subsurface site. The electronic structures of the H-adsorbed TaC(111) and NbC(111) surfaces are investigated by off-normal-emission measurements, and it is found that the surface electronic structures are similar to those of the original clean surfaces; the two-dimensional band structures of the H-modified surface states are similar to those for the intrinsic surface states on both surfaces. A possible hydrogen adsorption site in the subsurface region is also proposed.

I. INTRODUCTION

Transition-metal nitrides and carbides (TMNC's) are of considerable interest because of an interesting combination of physical properties and a number of useful applications. They exhibit an ultrahigh hardness, a high melting point as well as a metallic conductivity, and some of them are superconductors at fairly high temperature. From a practical point of view, they have been used as catalysts, field electron emitters, coating materials, etc., thus their surface properties are of particular interest. However, in contrast to the case for elemental metal and semiconductor surfaces, limited information has been available concerning gas adsorption on well-defined surfaces of TMNC's.

The interaction of hydrogen with metal surfaces is an important topic because of the technological importance of metal-hydrogen systems (embrittlement, catalysis, and hydrogen storage), and because the metal-hydrogen system has been viewed as a simple prototype system for studying chemical and physical processes at metal surfaces. Thus extensive studies on the hydrogen-metal surface interaction have so far been performed.[1–11] However, in contrast to substantial accumulation of data on hydrogen-metal systems, very limited information is available as to the hydrogen adsorption on well-defined surfaces of TMNC's. The fourth and fifth transition-metal carbides have a rock-salt structure, and it is known that the (111) polar surface is very active towards gas adsorption relative to other low-index surfaces.[12,13] Thus the (111) surface is of particular interest chemically, and a few H-adsorption studies have been performed on the TiC(111) surface. Oshima *et al.*[14] have performed electron-energy-loss spectroscopy (EELS) studies and have proposed that H is adsorbed on the threefold hollow site of the first Ti layer. Angle-resolved photoemission spectroscopy (ARPES) studies[15,16] have found that the chemisorption mechanism of H on the TiC(111) is similar to that for H/metal systems; the H 1*s*-induced split-off state is formed below the Ti 3*d*-*C* 2*p* valence band.

In this work, we report the results of the ARPES study with synchrotron radiation for the adsorption of hydrogen on the (111) surfaces of NbC and TaC. On these surfaces, the hydrogen adsorption induces an invisible phase at room temperature for H/TaC(111) and even at 80 K for H/NbC(111).

II. EXPERIMENT

Single crystals of $NbC_{0.9}$ and $TaC_{0.95}$ were grown by the floating-zone method at the National Institute for Research in Inorganic Materials.[17,18] The crystals with orientation (111) were cut by spark erosion into disks of 1-mm thickness, and subsequently polished mechanically. The (111) clean surfaces were prepared by flashing to about 1500 °C for NbC and to about 2000 °C for TaC in a vacuum chamber with the base pressure of 1×10^{-10} mbar. The (111) surfaces thus prepared both showed sharp (1×1) low-energy electron diffraction (LEED) patterns and no impurities were observed within the detection limit of Auger electron spectroscopy.

The ARPES measurements were made at the Photon Factory, National Laboratory for High Energy Physics. The experiments for the NbC(111) and the TaC(111) surfaces were performed using different chambers and beam lines. The experiments for the NbC(111) surface were

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made on Beam Line 11D where the synchrotron light was dispersed by a constant deviation monochromator. The chamber was equipped with an angle-resolved electron-energy analyzer of 150° spherical-sector type with an acceptance angle of ±1°. The total experimental (including the monochromator and electron-energy analyzer) energy resolution was ~0.2 eV. The NbC(111) sample was mounted onto a manipulator that permitted it to be cooled to 80 K with a liquid-N_2 cooling system. The sample was oriented so that the incidence plane was parallel to the $\langle 2\bar{1}\bar{1} \rangle$ azimuth. The experiments for the TaC(111) surface were made on Beam Line 11C where the synchrotron light was dispersed by a monochromator of Seya-Namioka type. The chamber was equipped with an angle-resolved analyzer (180° spherical-sector type) with an acceptance angle of ±1°. The total energy resolution was ~0.15 eV. The TaC(111) sample was mounted onto a manipulator, with which we could rotate the sample about the axis normal to the surface to change the detection plane of the sample, i.e., $\langle 01\bar{1} \rangle \Longrightarrow \langle 2\bar{1}\bar{1} \rangle$.

In this paper, the incidence angle of the (θ_i) and the detection angle of the photoelectron (θ_d) are given relative to the surface normal. The incident light was linearly polarized in the horizonal plane of incidence. In the ARPE spectra presented below, the electron binding energies are referenced to zero at the Fermi level (E_F) and spectra are normalized by photon flux estimated from the photocurrent of the final stage mirror.

III. RESULTS

First, we briefly discuss the atomic structure of the (111) surface of TaC and NbC. The (111) surface of a rock-salt-type crystal is a polar surface, and thus the first layer of the surface is a metal layer or a carbon layer. The LEED shows a sharp (1×1) pattern for both surfaces, indicating that any reconstructions are not brought about. The surface structure of TaC(111) has been studied by ion scattering spectroscopy, and it has been confirmed that the surface is covered with a Ta layer.[19] As for NbC(111), there has been no direct structural analysis, however, it has been proposed that the first layer is a Nb layer from the analysis of the surface electronic structure.[20] The details are discussed in our previous papers.[20]

A. H on TaC(111)

Figure 1 shows the change in the normal-emission spectrum for the TaC(111) surface as a function of hydrogen exposure at room temperature. The spectra were taken at $h\nu=25$ eV and $\theta_i=45°$.

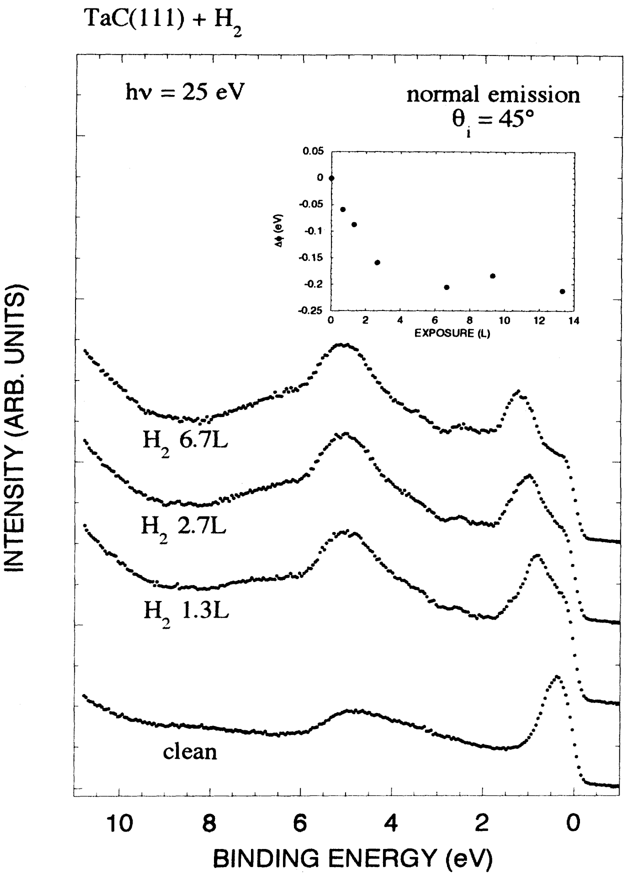

FIG. 1. Change in the normal-emission spectrum of the TaC(111) surface as a function of H_2 exposure at 300 K. The incidence angle of the light is 45°. The photon energy is 25 eV. Work-function change for the TaC(111) as a function of H_2 exposure is also inset.

First we discuss the interpretation of the spectrum for the TaC(111) clean surface. The spectrum is composed of a sharp peak at just below E_F and some broad bands at ≤9 eV. The sharp peak is shifted sensitively by a small amount of hydrogen exposure (Fig. 1). It is noted that we made $h\nu$-dependent ARPES measurements on the TaC(111) surface and confirmed that the peak showed no dispersion as a function of photon energy. These results indicate that this peak should be attributed to the emission from a surface-induced state. Previous ARPES studies have also shown that the surface-induced state is formed at just below E_F at the $\bar{\Gamma}$ point on the NbC(111) (Ref. 20) and TiC(111) (Refs. 15 and 21) surfaces. Fujimori *et al.*[22] made a theoretical study on the electronic structure of the TiC(111) surface, and have proposed that surface localized states derived from Ti 3*d* should be formed on this surface through a charge redistribution around the surface to screen a long-range electric field produced by the polar structure. The TaC(111) surface is also the polar surface, and the two-dimensional band dispersion of the surface-induced state determined by ARPES measurements (Fig. 4, which will also be discussed later) is well reproduced by the theoretical curve,[22] indicating that the state is derived from the Ta 5*d* orbitals of the surface Ta atoms and that the TaC(111) surface is also stabilized through the charge redistribution mechanism. Some broad bands at ≤9 eV are attributed to the emissions from Ta 5*d*-C 2*p* bulk bands. The observed band width (E_F—9 eV) is in good agreement with those estimated from the theoretical band curves along the Γ-*L* direction (8–9 eV) by Weinberger *et al.*[23] and Klein, Papaconstantopoulos, and Boyer.[24]

As the surface is exposed to H_2, some spectral changes are induced; the surface-induced state is shifted to the higher-binding-energy side and the emissions from bulk bands especially at < 5 eV are enhanced with the increase of H_2 exposure. For exposures larger than 6.7 L, no spectral change is observed, indicating that the saturation is reached at this exposure region. The work-function change ($\Delta\phi$) for the H/TaC(111) system as a function of hydrogen exposure is also shown in Fig. 1 as an inset. The $\Delta\phi$ is deduced from the secondary electron threshold in the photoemission spectra. The work function is decreased by ~ 0.2 eV after 6.7 L exposure. The LEED shows only a (1×1) pattern independently of the exposure.

The normal-emission spectra for the H/TaC(111) system are thus characterized by the absence of the H 1*s*-induced split-off state (Fig. 1). It is noted that broad emission is observed at ~ 7 eV after H adsorption, however, this should be associated with a bulk band emission enhanced by H adsorption since the emission shows $h\nu$-dependent dispersion. The H-induced enhancement of bulk band emissions will be discussed later. The adsorbed H is in the invisible state, though some spectral changes such as peak shift and emission enhancements are brought about by H adsorption. Previous photoemission studies for the H/metal systems have shown that the H 1*s*-induced state should be observed in the spectra when the H is adsorbed on the surface.[1–11] However, the invisible state has been also observed in some H/metal systems such as H/Pd(111), H/Ni(111),[2–4] and H/Ru(001) (Ref. 5) at room temperature, where it has been proposed that the H is adsorbed in subsurface (under layered) sites. The absence of the H 1*s*-induced state in the spectra for the subsurface adsorption state is more clearly shown for the H/Nb systems[7–9] where a reversible visible-invisible phase transition has been found according to the surface-subsurface site transition. Thus it is considered that the invisible state for the H/TaC(111) system should also be ascribed to the subsurface adsorption state. It is noted that, the H 1*s*-induced split-off state is clearly observed for the H/TiC(111) system,[16] where the H is confirmed to be located above the surface by an EELS study,[14] indicating that the state should be observable when the adsorbed H is on the surface even in the H/TMNC system.

As the TaC(111) is exposed to hydrogen, the surface-induced state, which is observed at 0.6 eV for the clean surface, is shifted towards the higher-binding-energy side (Fig. 1). After the saturation, the state is observed at 1.1 eV. It is noted that the state shifted by H adsorption does not show $h\nu$-dependent dispersion in the peak positions, indicating that the shifted state is also a surface localized state. The H-induced shifted state is called the extrinsic surface state, hereafter.

The surface-induced state shows a continuous shift as a function of hydrogen exposure (Fig. 1), indicating that

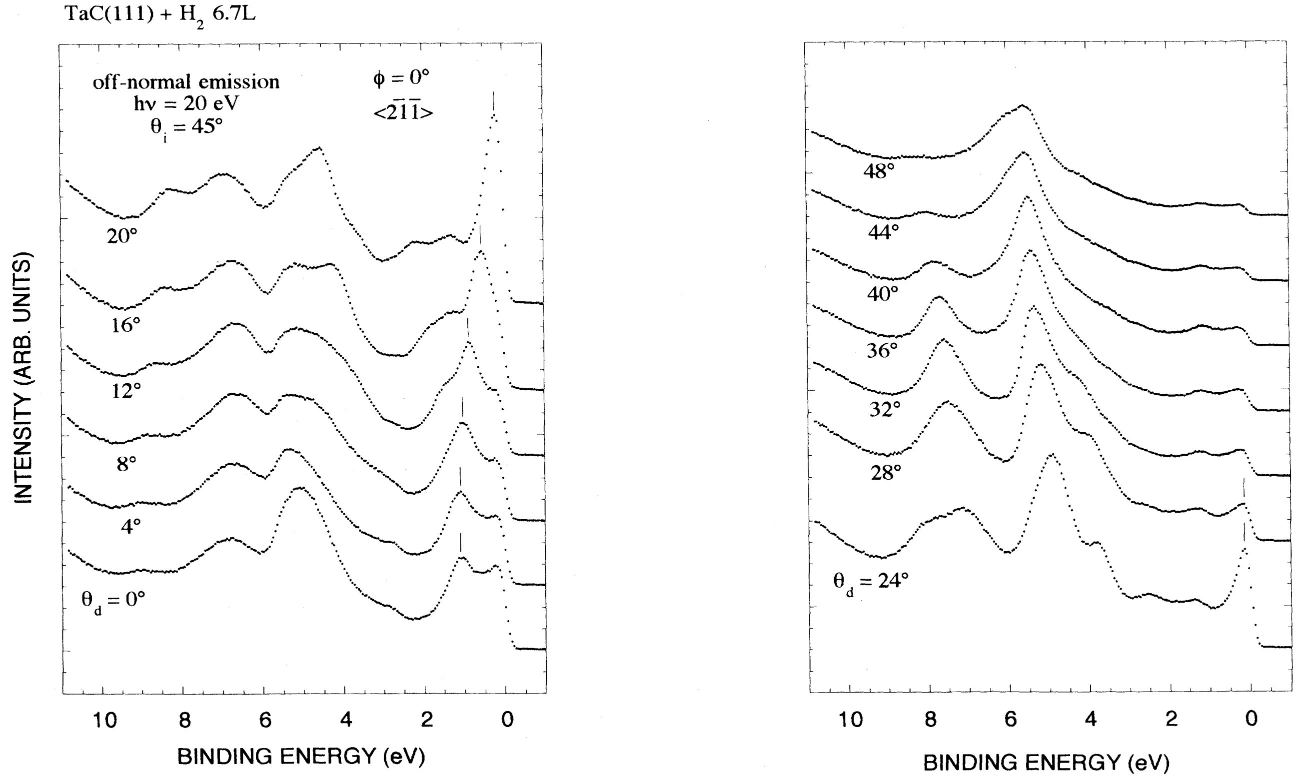

FIG. 2. Off-normal emission spectra for the TaC(111) surface exposed to 6.7 L H_2 along the $\langle 2\bar{1}\bar{1}\rangle$ direction. The photon energy is 20 eV and the incidence angle of the light is 45°.

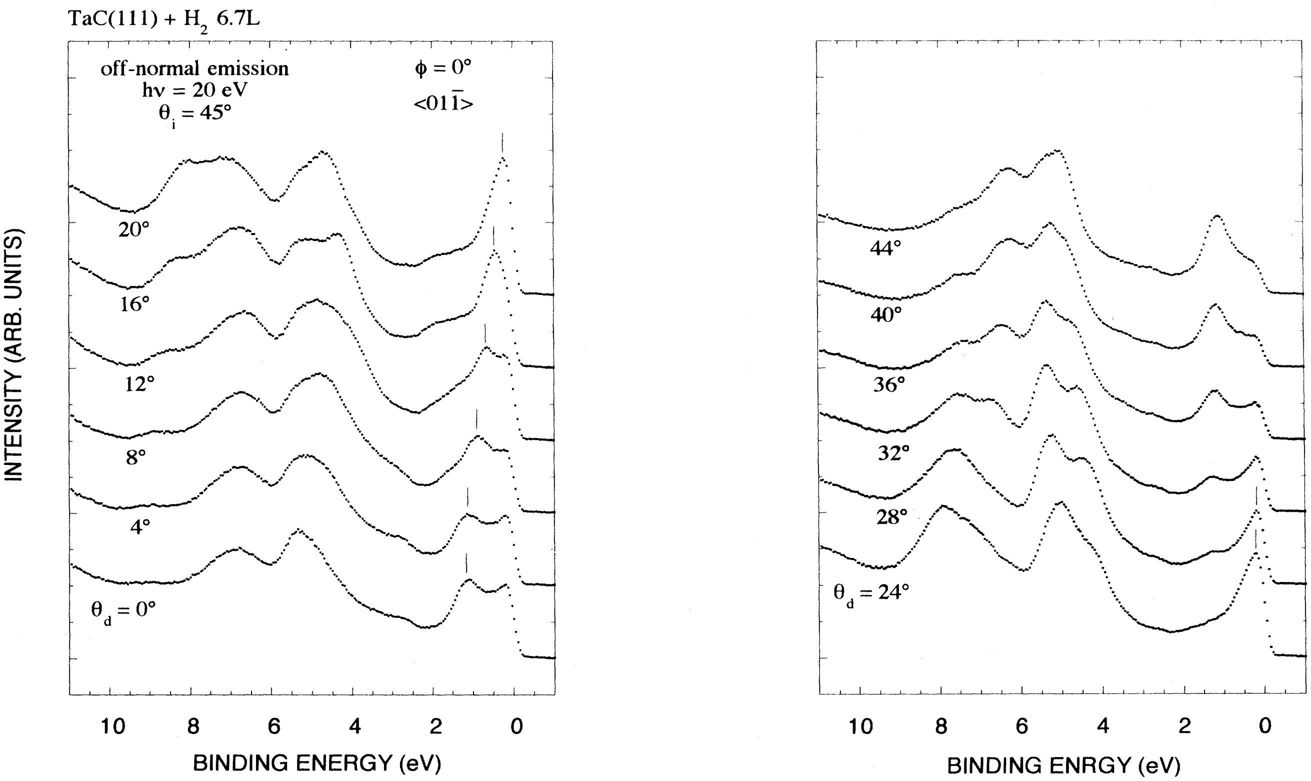

FIG. 3. Off-normal emission spectra for the TaC(111) surface exposed to 6.7 L H_2 along the $\langle 01\bar{1}\rangle$ direction. The photon energy is 20 eV and the incidence angle of the light is 45°.

the surface potential on the TaC(111) is continuously changed as a function of exposure. One of the possible reasons for this continuous potential change is that the adsorbed H atom is mobile to form a uniformly dense layer, as has been proposed for H/Ni(111) and H/Pd(111) systems.[4]

The two-dimensional band structure of a surface localized state can be deduced from off-normal-emission measurements. Figures 2 and 3 show off-normal-emission spectra for the TaC(111) surface saturated by hydrogen (6.7 L exposure) taken at various detection angles (θ_d) along the $\langle 2\bar{1}\bar{1}\rangle$ ($\bar{\Gamma}\bar{M}$) and $\langle 01\bar{1}\rangle$ ($\bar{\Gamma}\bar{K}$) directions, respectively. The spectra are taken at $h\nu=20$ eV and $\theta_i=45°$. It is seen from the spectra that the peak from

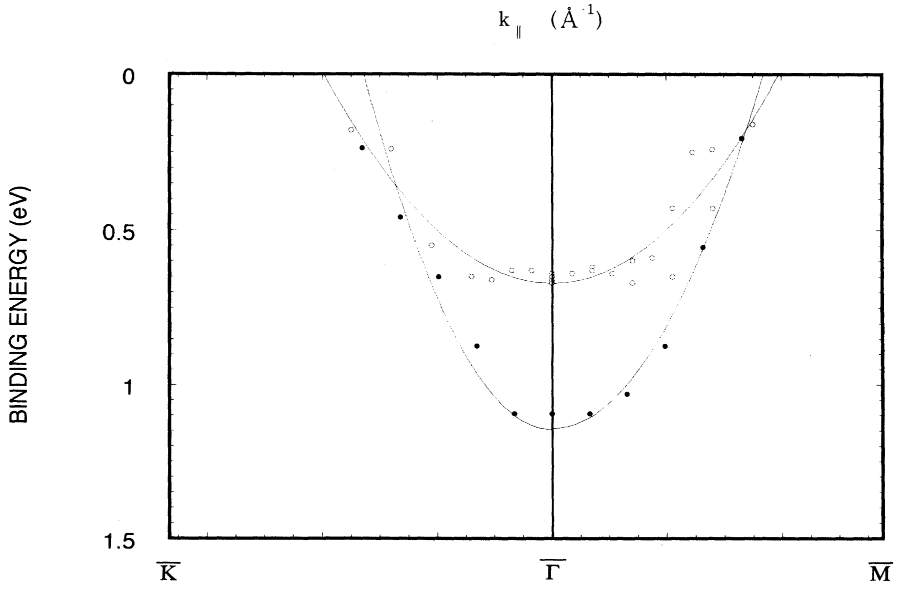

FIG. 4. Measured dispersion $E(k_\parallel)$ of the surface-induced state (○) for the clean surface and H-induced state (●) for the (1×1)H-TaC(111) system along the $\langle 2\bar{1}\bar{1}\rangle$ ($\bar{\Gamma}\bar{M}$) and $\langle 01\bar{1}\rangle$ ($\bar{\Gamma}\bar{K}$) directions.

the extrinsic surface state disperses upwards to cross the Fermi level as θ_d increases for both directions. The two-dimensional band structure $E(k_\parallel)$ can be mapped out using the relation between the parallel component of the detected wave vector ($\mathbf{k}_\parallel$) and the measured kinetic energy (E_{kin}), i.e.,

$$k_\parallel = \sqrt{2mE_{\mathrm{kin}}/\hbar^2}\sin\theta_d \ . \tag{1}$$

The results thus obtained in the $\bar{\Gamma}\bar{M}$ and $\bar{\Gamma}\bar{K}$ directions are summarized in Fig. 4. In Fig. 4, the results for the surface-induced state on the clean TaC(111) surface are also shown. The dispersion of the surface-induced state is very similar to that on the NbC(111) clean surface, which is reproduced in Fig. 7. This is due to the fact that the bulk electronic structures of NbC and TaC are very similar and that the same surface stabilization mechanism such as the charge redistribution[20,22] is operative for both NbC(111) and TaC(111) surfaces. As the TaC(111) surface is saturated by hydrogen, the surface-induced state is shifted to the higher-binding-energy side around the $\bar{\Gamma}$ point and the curvature of the band is increased (the effective mass is reduced from $m^*/m = 3.57$ to 1.82 for $\bar{\Gamma}\bar{M}$ and 3.60 to 1.43 for $\bar{\Gamma}\bar{K}$). This may be due to the increase of the $5d$-$5d$ interatomic overlapping after H adsorption, which may be caused by a through H interaction of the Ta $5d$ orbitals. Though the band structure of the surface-induced state is modified by H adsorption as described above, Fig. 4 shows that the overall surface electronic structure after H adsorption is similar to that for the clean surface; the half-filled metallic band of similar dispersion is existent on both surfaces.

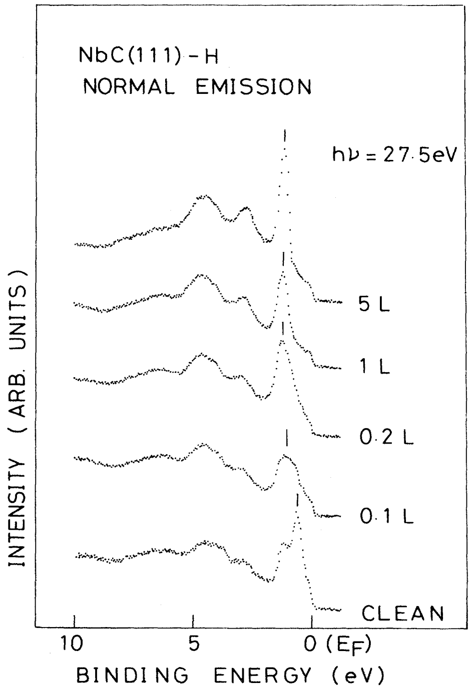

FIG. 5. Normal-emission spectra for the NbC(111) surface as a function of H_2 exposure at 80 K. The incidence angle is 60°. The photon energy is 27.5 eV.

B. H on NbC(111)

Figure 5 shows the change in the normal-emission ARPE spectrum of the NbC(111) surface as a function of hydrogen exposure at 80 K. The spectra are taken at $h\nu = 27.5$ eV ($\theta_i = 60°$). For more than 5 L exposure, no spectral change is observed, indicating that the saturation is reached at ~ 5 L exposure. As in the case of the H/TaC(111) system, only a (1×1) LEED pattern is observed independently of the hydrogen exposure.

The spectrum for the clean surface is similar to that for the TaC(111) surface; an intense emission is observed at just below E_F. The emission has been attributed to the emission from the surface-induced state which is characteristic for the (111) surface of transition-metal carbides.[20] The broad bands observed at ≤ 9 eV are ascribed to the bulk band emission. The detailed discussions about the spectra for the clean surface are given in our previous papers.[20]

As the surface is exposed to H_2, some spectral changes are induced; the emission from the surface-induced state is replaced by a H-induced peak which is at slightly higher binding energy (0.7→1.2 eV), and the bulk band emissions at < 5 eV are enhanced.

The spectra for the H/NbC(111) surface are character-

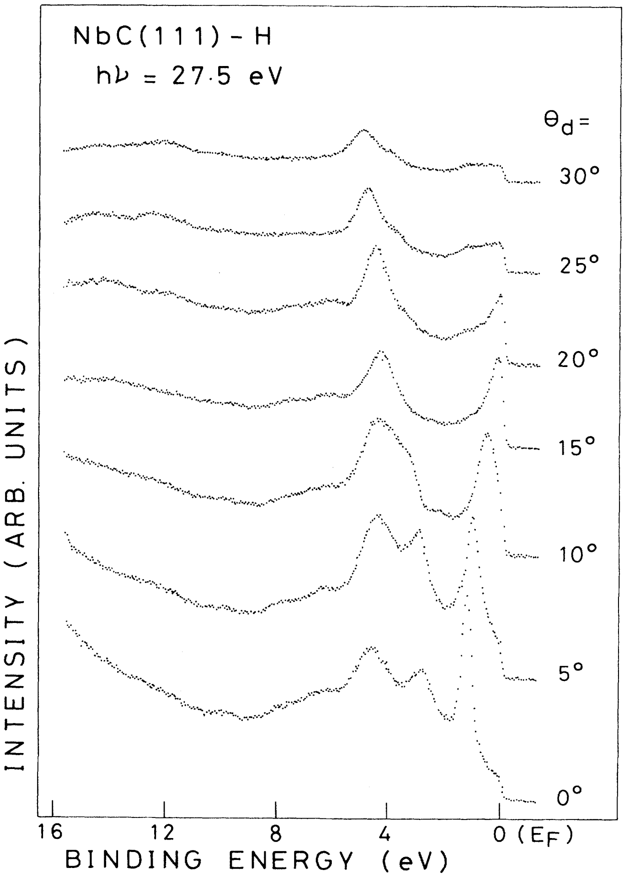

FIG. 6. Off-normal emission spectra for the NbC(111) surface saturated by H along the $\langle 2\bar{1}\bar{1}\rangle$ direction. The photon energy is 27.5 eV. The incidence angle of the light is 60°.

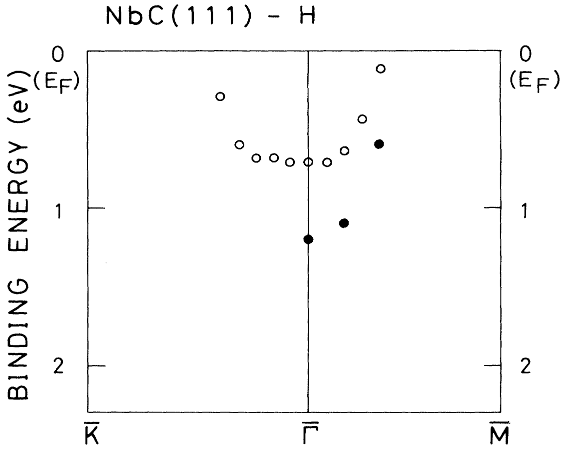

FIG. 7. Measured dispersion $E(k_\parallel)$ of the surface-induced state (○) for the clean surface and H-induced state (●) for the (1×1)H-NbC(111) system along the $\langle 2\bar{1}\bar{1}\rangle$ ($\bar{\Gamma}\bar{M}$) and $\langle 01\bar{1}\rangle$ ($\bar{\Gamma}\bar{K}$) directions.

ized by the absence of the H 1*s*-induced split-off state. It is surprising that the adsorbed H is in the invisible state even at 80 K. The electronic structure of the H/NbC(111) surface is very similar to that of the H/TaC(111) surface as discussed later, and thus the adsorbed site of H is attributed to a subsurface site also for the H/NbC(111) system.

Figure 6 shows off-normal-emission spectra for the NbC(111) surface saturated by H, taken at various detection angles along the $\langle 2\bar{1}\bar{1}\rangle$ ($\bar{\Gamma}\bar{M}$) azimuth. The spectra are taken at $h\nu=27.5$ eV and $\theta_i=60°$. The extrinsic surface state disperses upwards and crosses the Fermi level with the increase of θ_d. The two-dimensional band dispersion of the extrinsic surface state is plotted in Fig. 7 using an Eq. (1). The two-dimensional band structure of the intrinsic surface-induced state on the NbC(111) surface[20] is reproduced in Fig. 7. Though the dispersion only along the $\bar{\Gamma}\bar{M}$ direction is determined in this case, the electronic structure of the H/NbC(111) can be concluded to be very similar to that of the H/TaC(111) system (Fig. 4); the H-induced state is located at 1.2 eV at the $\bar{\Gamma}$ point around halfway between the $\bar{\Gamma}$ and $\bar{M}$ point, for both systems.

IV. DISCUSSION

Our photoemission data show that the adsorbed H is in the invisible state, and the state may be attributed to the (ad) absorption in a subsurface site for both TaC(111) and NbC(111) surface layers. The adsorbed H is however not far from the topmost surface because the surface electronic structure is much affected by H adsorption. Considering the decrease of the work function and the shifts of the surface-induced state, the adsorbed H is considered to be located just below the surface Ta or Nb layers. Hydrogen is known to be usually adsorbed in a high-symmetry site.[25] The high-symmetry sites (C_{3v}) just below the first metal layer are schematically shown in Fig. 8; (*A*) below metal threefold hollow site and on the second layer C atoms; (*B*) below metal threefold hollow site and on the third layer metal atoms, and (*C*) right below the first metal atoms. Unfortunately, it is difficult to decide the most suitable site directly from the present photoemission data. However, it is noted that, H adsorption enhances the bulk band emissions especially at <5 eV for both H/TaC(111) and H/NbC(111) systems. The enhancement of the bulk band emission due to H adsorption has also been found for H/Ni(111) system,[27] where the enhancement is explained by the change of the matrix element at the surface. A previous theoretical study on the electronic structure of NbC cluster has shown that the lower and higher binding energy parts of the Nb 4*d*-C 2*p* valence bands are mainly composed of Nb 4*d* and C 2*p* components, respectively.[28] Our photoemission data show that the Nb 4*d* (Ta 5*d*)-C 2*p* valence bands are observed at 0–9 eV, and the emission only at <5 eV are enhanced, indicating that the matrix elements of mainly Nb 4*d* and Ta 5*d* components are affected by H adsorption. Thus, assuming that the enhancement of the emission is caused by the H-mediated enhancement of matrix element of the metal *d* bands, it is not likely that adsorbed H occupies the site *A*; on top of the bulk carbon atom, where the adsorbed H should have little effect on the matrix element of metal *d* orbital. In site *C* the adsorbed H is completely hidden by the surface metal atom and does not affect the matrix element at the surface.

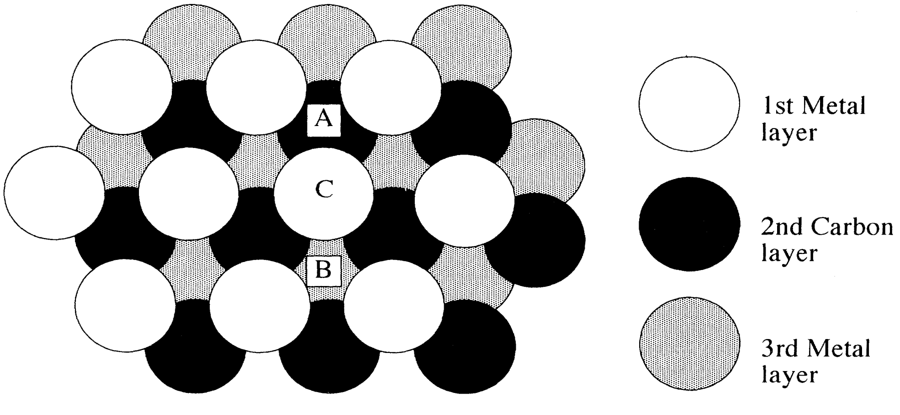

FIG. 8. High-symmetry site of the TaC and NbC(111) surface; (*A*) below metal threefold hollow site and on the second layer C atoms, (*B*) below metal threefold hollow site and on the third layer metal atoms, and (*C*) right below the first metal atoms.

Thus we tentatively attribute the adsorption site to the site *B* where adsorbed H sits on the bulk metal atom and thus can have some effects on the matrix element of the bulk metal *d* orbitals.

The adsorption of hydrogen in the invisible state is not a characteristic common property to all the transition-metal carbide (111) surfaces. Our previous ARPES study for the H/TiC(111) system has found that a H 1*s*-induced split-off state is formed below the Ti 3*d*-C 2*p* valence band.[16] Oshima *et al.*[14] has determined the adsorption site to be on the threefold hollow site by an EELS study in the case of the H/TiC(111) system. Thus the potential-energy curves around the surface for the hydrogen adsorption-sorption process are not common to the TiC and NbC, TaC(111) surfaces. It is difficult to draw the exact potential-energy curve, however, it is considered that the subsurface site is in a more electron rich condition for NbC and TaC than in that for TiC because of large spatial extension of 4*d* and 5*d* orbitals relative to 3*d* orbitals, which may make the adsorption site more attractive to hydrogen atoms.

V. SUMMARY

Angle-resolved photoemission measurements have been performed to study the interaction of hydrogen with TaC(111) and NbC(111) surfaces. For the clean surfaces, the photoemission spectra for both surfaces are characterized by the emission from the surface-induced state at just below E_F. ARPES measurements show that these surface-induced states have very similar two-dimensional band structures, which are qualitatively reproduced by a theoretical curve for the TiC(111) by Fujimori, Minami, and Tsuda.[22] As the surface is exposed to H_2, only (1×1) LEED patterns are observed on both surfaces independently of the exposure. The H 1*s*-induced split-off state is not found for both surfaces, thus the adsorbed H forms an invisible state. For the H/TaC(111) system, the $\Delta\phi$ is measured as a function of H_2 exposure, and it is found that the work function is decreased by ~0.2 eV by H adsorption. Considering these results, the adsorbed site is proposed to be a subsurface site. The surface-induced states are shifted to higher-binding-energy side by H adsorption at the $\overline{\Gamma}$ point on both surfaces. The band structures of the H-induced states are determined by ARPES measurements and it is found that these are very similar to each other on the TaC(111) and NbC(111) surfaces, and also to those for the intrinsic surface-induced state.

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